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(71)Applicant : YUASA CORP

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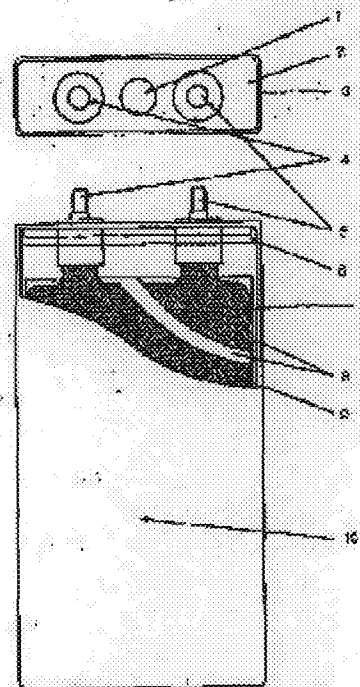
(72)Inventor : OKABE KAZUYA  
SHIOZAKI RYUJI  
YUFU HIROSHI

(54) POSITIVE ACTIVE MATERIAL AND NONAQUEOUS ELECTROLYTE SECONDARY BATTERY USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive active material capable of manufacturing a nonaqueous electrolyte secondary battery with excellent high rate discharge performance and charge/discharge cycle performance, high safety, and high energy density, and to provide a nonaqueous electrolyte secondary battery using the positive active material.

SOLUTION: This positive active material contains a compound oxide represented by composition formula,  $\text{Li}(1+a)[\text{Mn}_x\text{Ni}_y\text{Co}_z\text{Mb}]\text{O}_2$  (M is an element other than Mn, Ni, Co, and Li), and the coefficients in the composition formula satisfy the following relations. Moreover, the nonaqueous electrolyte secondary battery has a positive electrode containing the positive active material as the main component, a separator, and a negative electrode. [In the composition formula,  $0 \leq a \leq 0.1$ ,  $-0.1 \leq x-y \leq 0.1$ ,  $y \leq x+z+b$ ,  $0 < z \leq 0.4$ ,  $0.3 \leq x$ ,  $0.3 \leq y$ , and  $x+y+z+b=1$ .].



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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to positive active material and the nonaqueous electrolyte secondary battery which used this.

[0002]

[Description of the Prior Art]Nonaqueous electrolyte secondary batteries, such as a lithium secondary battery, show a high energy density, and since they are high tension, they are widely used as a power supply to a small personal digital assistant, a mobile communication apparatus, etc. It is required for the positive active material for lithium secondary batteries also by repetition of insertion and desorption of lithium that a crystal structure should be stable and electrochemical operation capacity should be large.

[0003]Operating potential as a thing of the 4V neighborhood now The lithium cobalt oxide ( $\text{LiCoO}_2$ ) and lithium nickel oxide ( $\text{LiNiO}_2$ ) of the layer structure, Or the multiple oxide of lithium and the transition metal which make basic constitution a lithium manganic acid ghost ( $\text{LiMnO}_2$  and  $\text{LiMn}_2\text{O}_4$ ) with Spinel structure, etc. is known. Although the lithium cobalt multiple oxide expressed with  $\text{LiCoO}_2$  etc. also in the positive active material which has the  $\alpha\text{-NaFeO}_2$  structure where these high energy density is expectable is widely used for the noncommercial lithium ion battery etc., Cobalt is a rare metal and there was a problem that a price was high. Since it lacks in the stability in an elevated temperature, and reservation of safety is difficult for the lithium nickel complex oxide expressed with  $\text{LiNiO}_2$  etc., it has not resulted in utilization.

Although the lithium manganic acid ghost which has the Spinel structure expressed with  $\text{LiMn}_2\text{O}_4$  etc. is cheap and it is the positive active material excellent also in safety, Although the energy density per weight is only about 70% compared with a lithium cobalt multiple oxide and utilization is carried out partly, it has not come to be used widely on a noncommercial way.

[0004]On the other hand, since high capacity can be expected theoretically and it excels also in safety,  $\text{LiMnO}_2$  has been examined widely. The monoclinic form structure of having the rhombic system structure of having  $\beta\text{-NaMnO}_2$  structure, and the  $\alpha\text{-NaMnO}_2$  structure which is stratified halite structure as a

structure of said  $\text{LiMnO}_2$  is known.

[0005] Although  $\text{LiMnO}_2$  of said rhombic system structure could expect capacity higher than said  $\text{LiMn}_2\text{O}_4$ , when charge and discharge were repeated, since the rearrangement to a spinel phase arose gradually, there was a problem of being inferior to the stability to a charging and discharging cycle.  $\text{LiMnO}_2$  of said monoclinic structure, That high charge-and-discharge performance is not enough, and the capacity lowering accompanying a charging and discharging cycle is also large, For example, Chiang, Y-M.; Sadoway, D.R.; Jang, Y-I.; Huang, B.; Wang, H. High Capacity, Temperature-Stable Lithium Aluminium Manganese It is reported to Oxide Cathodes for Rechargeable Batteries. *Electrochem. Solid-State Lett.* 2 (3), 1999, and 107-110.

[0006] In order to solve these problems, Mn of  $\text{LiMnO}_2$  aluminum, The amount substitution of 1-y ( $0.5 \leq y \leq 1$ ) is carried out by Fe, Co, nickel, Mg, or Cr, And the seal of approval of the voltage of 4.0V-4.8V is carried out at 60-100 \*\* between an anode and a negative electrode, change of a crystal structure is accelerated, and the art of improving a high charging and discharging characteristic is indicated (refer to JP,2001-23617,A). However, even if it used such art, in addition, the high charging and discharging characteristic was not enough.

[0007] Said lithium manganic acid ghost has many technical issues which should be conquered in the use. There was a problem that the cycle performance and preservation performance especially at the time of an elevated temperature were inferior.

[0008]

[Problem(s) to be Solved by the Invention] This invention was made in order to solve the above-mentioned problem, and it is \*\*\*\*. The purpose is to provide the nonaqueous electrolyte secondary battery using the positive active material and this which can produce the nonaqueous electrolyte secondary battery of the high energy density which is excellent in performance and charge-and-discharge cycle performance, and has high safety.

[0009]

[Means for Solving the Problem] In order to attain the above-mentioned technical problem, as a result of inquiring wholeheartedly, by using a multiple oxide which has a specific presentation as positive active material, this invention persons found out that a cell provided with a battery characteristic excellent in a surprising thing was obtained, and resulted in this invention. That is, engineering construction of this invention is attained by the following. Presumption is included about the mechanism of action made in this specification, and right or wrong of the mechanism of action do not restrict this invention.

[0010] positive active material concerning this invention was indicated to claim 1 -- as -- empirical formula  $\text{Li}_{(1+a)}[\text{Mn}_x\text{nickel}_y\text{Co}_z\text{M}_b]\text{O}_2$  (M -- Mn.) It is expressed by elements other than nickel, Co, and Li, and a coefficient in said empirical formula contains a multiple oxide which fills the following expression of relations.

$0 \leq a \leq 0.1$ ,  $0.1 \leq x-y \leq 0.1$ ,  $y \leq x+z+b$ ,  $0 < z \leq 0.4$ ,  $0.3 \leq x$ ,  $0.3 \leq y$ ,  $x+y+z+b=1$  -- according to such composition. It excels in high charge-and-discharge performance and charge-and-discharge cycle performance, and can be

considered as positive active material which can produce a nonaqueous electrolyte secondary battery of high energy density which has high safety.

[0011]Positive active material concerning this invention is characterized by obtaining a multiple oxide by being calcinated for 3 hours or more at not less than 900 °C the temperature of 1100 °C or less, as indicated to claim 2. According to such composition, it can be considered as positive active material which can produce a nonaqueous electrolyte secondary battery excellent in especially initial capacity and charge-and-discharge cycle performance.

[0012]This invention persons found out that a nonaqueous electrolyte secondary battery excellent in especially high rate discharge performance was producible, when said M was at least one sort of elements chosen from a group which consists of B, aluminum, Mg, Cr, and Fe. Therefore, positive active material concerning claim 3 is characterized by M being at least one sort of elements chosen from a group which consists of B, aluminum, Mg, Cr, and Fe.

[0013]Positive active material concerning this invention is characterized by specific surface area by a BET adsorption method of a multiple oxide being 0.3-1.5m<sup>2</sup>/g, as indicated to claim 4. According to such composition, it can be considered as positive active material which can produce a nonaqueous electrolyte secondary battery excellent in especially a high rate discharging characteristic and charge-and-discharge cycle performance.

[0014]As indicated to claim 5, positive active material concerning this invention a multiple oxide, 2 theta of a powder X-ray diffraction figure which uses CuK alpha rays 18.6° degree, It is characterized by being a crystal structure which has a peak at 36.6° degree, 37.8° degree, 38.2° degree, 44.3° degree, 48.4° degree, 58.4° degree, 64.2° degree, 64.8° degree, and 68.8° degree. According to such composition, it can be considered as positive active material which can produce a nonaqueous electrolyte secondary battery excellent in especially charge-and-discharge cycle performance.

[0015]As positive active material concerning this invention was indicated to claim 6, hue of a multiple oxide is characterized by a chromaticity of a red direction being low as compared with JIS standard color chart Y05-30B. According to such composition, especially capacity of charge and discharge can consider it as positive active material which can produce a nonaqueous electrolyte secondary battery secured certainly.

[0016]Since according to the nonaqueous electrolyte secondary battery concerning this invention it is characterized by providing an anode, a separator, and a negative electrode which use positive active material concerning this invention as a major constituent as indicated to claim 7, It excels in high charge-and-discharge performance and charge-and-discharge cycle performance, and can be considered as a nonaqueous electrolyte secondary battery of high energy density which has high safety.

[0017]

[Embodiment of the Invention]Hereafter, this invention is explained in detail. The nonaqueous electrolyte battery concerning this invention comprises an anode which uses positive active material as a major constituent, a negative electrode which uses a carbonaceous material as a major constituent, and nonaqueous electrolyte which electrolyte salt contained in the nonaqueous solvent, and, generally a separator is formed between an anode and a negative electrode.

[0018]In this invention, the positive active material which constitutes an anode, It is expressed with empirical

formula  $\text{Li}_{(1+a)}[\text{Mn}_x\text{nickel}_y\text{Co}_z\text{M}_b]\text{O}_2$  (M is elements other than Mn, nickel, Co, and Li), and the coefficient in said empirical formula makes it requirements to contain the multiple oxide which fills the following expression of relations.

$0 \leq a \leq 0.1$   $-0.1 \leq x-y \leq 0.1$   $y \leq x+z+b$   $0 < z \leq 0.4$   $0.3 \leq x \leq 0.3$   $x+y+z+b=1$  [0019] The above-mentioned empirical formula chose nickel which can expect high service capacity as an element in which this invention person etc. replace Mn paying attention to  $\text{LiMnO}_2$  which shows the comparatively outstanding cycle performance next. The result checked that action potential called 4.3V-3.0V is obtained, and that high service capacity called 140 mAh/g was obtained in  $\text{LiMn}_{0.5}\text{nickel}_{0.5}\text{O}_2$  which made the amount of substitution 50%. [excellent in compatibility with the conventional lithium ion battery] However, there was little capacity compared with  $\text{LiCoO}_2$  and charge-and-discharge cycle performance and the high charge-and-discharge performance were not enough. Then, the firing condition at the time of this invention persons compounding  $\text{LiMn}_{0.5}\text{nickel}_{0.5}\text{O}_2$ . When examination is wholeheartedly repeated about kinds, composition ratios, etc. of a dissimilar metal element other than Li to add, Mn, and nickel, despite the multiple oxide of the same presentation according to a firing condition. The color of crystal powder and the structure of a crystal which are acquired differed from each other greatly, and it turned out that service capacity and charge-and-discharge cycle performance are greatly improvable depending on the gestalt of a crystal. And try improvement in service capacity further and  $\text{LiMn}_{0.5}\text{nickel}_{0.5}\text{O}_2$  of said structure is made into a basic skeleton, As a result of examining wholeheartedly the system which added different species elements other than Mn and nickel, to a surprising thing. When Co is chosen as said dissimilar metal element, it finds out and determines to improve greatly also about high charge-and-discharge performance with the large improvement in the service capacity that the service capacity of 160 - 165 mAh/g is specifically obtained. It is thought that charge-and-discharge capacity of this improved as a result of are effective in stabilizing structure and the abstraction reaction of lithium from a crystal structure thing advancing easily with more \*\*\*\* potential for this reason when Co is added and also.

[0020] In the above-mentioned empirical formula, when satisfying  $0 \leq a \leq 0.1$ , a crystal grows easily at the time of calcination, and firing time can be shortened. Preferably, a is 0 or more and 0.04 or less. When there is less Li than zero, probably in order to make the internal resistance of a cell increase, service capacity is no longer obtained hardly. if a becomes large on the other hand -- 0.1 -- until -- although service capacity is maintained, the tendency for high rate discharge performance to fall is obtained. That is, it is easy to corn, when the specific surface area of positive active material falls, the internal resistance of a cell increases, and what added many Li(s) is considered that the capacity at the time of high rate discharge falls.

[0021] In the above-mentioned empirical formula, when only in the case of  $-0.1 \leq x-y \leq 0.1$  a stable crystal structure is acquired and it satisfies the expression of relations of  $y \leq x+z+b$ , high safety is obtained. Said safety is so high that the value of  $x+z+b$  is large, and is 0.6 or more preferably. These expressions of relations control the quantity of nickel which constitutes a multiple oxide under a specific condition, and can use it as the positive active material provided also with high safety by this.

[0022] moreover -- in the above-mentioned empirical formula --  $0 < z \leq 0.4$  -- z is 0.3 or less preferably.

Although this expression of relations specifies the quantity of Co (cobalt), Co promotes crystallization in a

small quantity, and although it has the effect of making capacity increasing dramatically, since safety becomes unstable so that it increases, it needs to be taken as a mentioned range.

[0023]Although it makes to be  $0.3 \leq x$  and to be  $0.3 \leq y$  into requirements in the above-mentioned empirical formula, If this has too little quantity of Mn (manganese), it has the tendency for safety to fall probably because the characteristic of  $\text{LiNiO}_2$  excels when  $x$  is too small, and  $y$  is too small, There is too little quantity of nickel (nickel) and it is because there is a tendency for charge-and-discharge cycle performance to fall probably because the characteristic of  $\text{LiMnO}_2$  excels.

[0024]It is  $x+y+z+b=1$ . This is because it is required in order to maintain the layer structure with a stable multiple oxide. Although the composition ratio of Li is  $1+a$ , this is the composition ratio after calcination.

[0025]Especially if the different species elements M which constitute the above-mentioned empirical formula are elements other than Mn, nickel, Co, and Li, it is not limited, but the element which can be replaced by Mn is preferred. For example, B, Be, V, C, Si, P, Sc, Cu, Zn, Ga, germanium, As, Se, Sr, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, Ta, W, Pb, Bi, Fe, Cr, Ti, Zr, Nb, Y, aluminum, Na, K, Mg, Ca, Cs, La, Ce, Nd, Sm, Eu, Tb, etc. are mentioned. Especially, since an effect especially remarkable in high rate discharge performance will be acquired if either B, aluminum, Mg, Cr or Fe is used, it is especially desirable.

[0026]In order that these different species elements M may improve a high charging and discharging characteristic, they are used in order to shift a presentation intentionally, and it is preferred about the quantity to satisfy  $z+b < x+y$  in addition to satisfying the above-mentioned expression of relations. It is preferred to satisfy  $0 < z+b \leq 0.4$  especially and it is preferred to especially satisfy  $0.05 \leq b$ . By satisfying these formulas can show higher safety.

[0027]Although it is not necessarily clear about this operation effect, since the size of said different species element differs from the size of Mn element or nickel element, the layer structure which constitutes positive active material is influenced, it has influence to the moving trucking of Li ion, and it is thought that the effect which makes ion conduction good was brought about. It is thought that they eased the expansion shrinkage distortion of the active material crystal accompanying charge and discharge by existence of the element in which sizes differ since different species elements other than Mn and nickel differed in the atomic radius of the element, i.e., a size.

[0028]As for the multiple oxide expressed with the above-mentioned empirical formula, it is preferred that the specific surface area by a BET adsorption method is  $0.3\text{--}1.5\text{m}^2/\text{g}$ . Although there is no problem in charge-and-discharge cycle performance when specific surface area is too low, when there is a tendency for high rate discharge performance to be inferior and specific surface area becomes high too much conversely, there is a tendency for charge-and-discharge cycle performance to be inferior. therefore, the thing for which specific surface area is made into a mentioned range -- the performance which combines the more outstanding high rate discharging characteristic and high cycle performance can be obtained.

[0029] $2\theta$  of the powder X-ray diffraction which uses CuK alpha rays the multiple oxide used for this invention  $18.6^{\circ}$ , It is preferred that it is a crystal structure which has a peak at  $36.6^{\circ}$ ,  $37.8^{\circ}$ ,  $38.2^{\circ}$ ,  $44.3^{\circ}$ ,  $48.4^{\circ}$ ,  $58.4^{\circ}$ ,  $64.2^{\circ}$ ,  $64.8^{\circ}$ , and  $68.8^{\circ}$  degree. When it has this crystal structure, the outstanding cycle performance is obtained. Although it is not clear about this operation effect, it is thought that the crystal in which said

powder X-ray diffraction pattern is shown is because it is low-skew and the structure of a crystal itself is stable.

[0030]The thing whose chromaticity of a red direction is [ the hue of the multiple oxide used for this invention ] low as compared with JIS standard color chart Y05-30B (Munsell-value 5R3/1) is preferred. Here, "the chromaticity of a red direction is low" shows that red is thin. When the chromaticity of a red direction is low (it is not red), calcination comes out enough and means a certain thing, There is a tendency for high capacity to be obtained more on the occasion of charge and discharge, when the chromaticity of a red direction is conversely high in hue (red), since calcination is insufficient or Li and nickel volatilize by calcination, it means that the presentation has shifted, and there is a tendency for the capacity of charge and discharge to decrease.

[0031]The particle diameter of the multiple oxide which is a main constitution substance of the positive active material used for this invention, taking into consideration the coating nature at the time of electrode production, since specific surface area increases so that it is small, it becomes easy to come out of output characteristics and the fall of other performances, especially preservation performance is prevented, although not limited -- particle diameter  $D_{50}$  = -- it is desirable that it is 9-10 micrometers preferably 5-30 micrometers. Particle diameter does not show the primary particle particle diameter of a crystal, and shows the particle diameter of secondary particles.

[0032]If the multiple oxide used for this invention has the above-mentioned empirical formula and the above-mentioned expression of relations is satisfied, although the manufacturing method in particular is not what is limited -- Li, Mn, nickel, Co, and M -- fine -- the method of grinding and calcinating, the method of changing pH and making the raw material which dissolved in aqueous acids coprecipitate, etc. are mentioned. Preferably, since preferably makes element substitution perfect, in order to make specific surface area small moderately by the granulation at the time of calcination, a thing for 10 hours or more is preferred [ in order to perform element substitution thoroughly, it is not less than 950 \*\* and 1100 \*\* or less which control of Li volatilization at the time of calcination tends to carry out, and ] for 3 hours or more.

[0033]Electrolyte salt usually contains the nonaqueous electrolyte which constitutes the nonaqueous electrolyte secondary battery of this invention in a nonaqueous solvent, and it is usable in what the use to a lithium cell etc. is generally proposed as. As a nonaqueous solvent, for example Propylene carbonate, ethylene carbonate, Cyclic carbonate, such as butylene carbonate, chloroethylene carbonate, and vinylene carbonate; Gamma-butyrolactone, Cyclic ester, such as gamma-valerolactone; Dimethyl carbonate, diethyl carbonate, Chain carbonate, such as ethyl methyl carbonate; Methyl formate, methyl acetate, chain ester species [ , such as methyl butyrate, ]; -- tetrahydrofuran or its derivative; -- 1,3-dioxane, 1,4-dioxane, 1,2-dimethoxyethane, 1,4-dibutoxyethane, Ether, such as a methyl jig lime; although nitril; dioxolanes, such as acetonitrile and benzonitrile, or the derivative; ethylene sulfide of those, sulfolane, a sultone, or its derivative can be independent or these two or more sorts of mixtures etc. can be mentioned, It is not limited to these.

[0034]As electrolyte salt, for example,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiPF}_6$ ,  $\text{LiSCN}$ ,  $\text{LiBr}$ ,  $\text{LiI}$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ ,  $\text{NaClO}_4$ ,  $\text{NaI}$ ,  $\text{NaSCN}$ ,  $\text{NaBr}$ , The inorganic ion salt containing one sort of lithium (Li), such as  $\text{KClO}_4$  and  $\text{KSCN}$ , sodium (Na), or potassium (K),  $\text{LiCF}_3\text{SO}_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)$

$(C_4F_9SO_2)_3Li$ ,  $(CF_3SO_2)_3Li$ ,  $(C_2F_5SO_2)_3Li$ ,  $(CH_3)_4NBF_4$ ,  $(CH_3)_4NBr$ ,  $(C_2H_5)_4NClO_4$ ,  $(C_2H_5)_4NI$ ,  $(C_3H_7)_4NBr$ ,  $(n-C_4H_9)_4NClO_4$ ,  $(n-C_4H_9)_4NI$ ,  $(C_2H_5)_4N$ -maleate,  $(C_2H_5)_4N$ -benzoate,  $(C_2H_5)_4N$ -phthalate, stearylsulfonic acid lithium, octylsulfonic acid lithium, and lithium dodecylbenzenesulfonate, etc. are mentioned, it is possible independence or for two or more kinds to be mixed and to use these ionic compounds.

[0035]By mixing and using  $LiBF_4$  and the lithium salt which has a perfluoroalkyl group like  $LiN(C_2F_5SO_2)_2$ , Since electrolytic viscosity can furthermore be lowered, the low-temperature characteristic can be improved further and it is more desirable.

[0036]In order to obtain certainly the nonaqueous electrolyte battery which has a high battery characteristic as concentration of the electrolyte salt in nonaqueous electrolyte, 0.1 mol/l - 5 mol/l are 1 mol/l - 2.5 mol/l desirable still more preferably.

[0037]The electrode by which the electrode which comprised an above-mentioned specific multiple oxide was constituted from high graphite of the degree of graphitization with the sufficient carbonaceous material, especially initial charging efficiency to a negative electrode is suitably used for the anode of the nonaqueous electrolyte secondary battery of this invention.

[0038]adding to the multiple oxide mentioned above as positive active material which is a major constituent of an anode -- other lithium containing transition metal oxides etc. -- since a high energy density and high safety will be obtained if independent, it mixes and it uses, it is desirable. As other lithium containing transition metal oxides, general formula  $Li_xMX_2$  and  $Li_xMn_yX_2$  (M.) N shows the metal of a group VIII from I, and X shows chalcogen compounds, such as oxygen and sulfur. It is, For example,  $Li_yCo_{1-x}M_xO_2$ ,  $Li_yMn_{2-x}M_xO_4$  (as for M, the metal (for example, one or more kinds of elements of Li, Ca, Cr, nickel, Fe, and Co) of a group VIII, etc. are mentioned from I.) Although it is effective to the peak which can be replaced about x value which shows the amount of different species element substitution of this lithium containing transition metal oxide, it is  $0 \leq x \leq 1$  from a point of service capacity preferably. About y value which shows lithium volume, the peak which can use lithium reversibly is effective, and it is  $0 \leq y \leq 2$  from a point of service capacity preferably. Although mentioned, it is not limited to these.

[0039]May mix to the multiple oxide by this invention further, may use other positive active material for it, and as other positive active material, I group metal compounds, such as  $CuO$ ,  $Cu_2O$ ,  $Ag_2O$ ,  $CuS$ , and  $CuSO_4$ , Group IV metallic compounds, such as  $TiS_2$ ,  $SiO_2$ , and  $SnO$ , V group metal compounds, such as  $V_2O_5$ ,  $V_6O_{12}$ ,  $VO_x$ ,  $Nb_2O_5$ ,  $Bi_2O_3$ , and  $Sb_2O_3$ , VI group metallic compounds, such as  $CrO_3$ ,  $Cr_2O_3$ ,  $MoO_3$ ,  $MoS_2$ ,  $WO_3$ , and  $SeO_2$ , VII group metal compounds, such as  $MnO_2$  and  $Mn_2O_3$ , . Are expressed by group VIII metal compounds, such as  $Fe_2O_3$ ,  $FeO$ ,  $Fe_3O_4$ ,  $nickel_2O_3$ ,  $NiO$ ,  $CoO_3$ , and  $CoO$ , etc. To metallic compounds, such as a lithium cobalt system multiple oxide and a lithium manganese system multiple oxide, and a pan, for example, conductive polymer compounds, such as disulfide, polypyrrole, poly aniline, poly para-phenylene, polyacethylene, and poly acene system material. Although a pseudo-graphite structure carbonaceous material etc. are mentioned, it is not limited to these.

[0040]An anode is suitably produced by applying or sticking this positive electrode mixture to foil, the Russ board, etc. as a charge collector by pressure, and heat-treating a multiple oxide at the temperature of 50 \*\* - about 250 \*\* for about 2 hours, after kneading with a filler if needed further and considering it as positive electrode mixture, a conducting agent and a binder, and.

[0041]As a negative pole material, a lithium metal, a lithium alloy (lithium metal content alloys, such as lithium aluminum, lithium lead, lithium tin, lithium aluminum tin, lithium gallium, and a Wood metal), etc. The alloy which can emit [ occlusion and ] lithium, carbon materials (for example, graphite, hard carbon, low-temperature-baking carbon, amorphous carbon, etc.), etc. are mentioned. Also in these, since it can lessen self-discharge and can lessen irreversible capacity in charge and discharge when lithium salt is adopted as electrolyte salt, since graphite has the action potential very near metal lithium, it is preferred as a negative pole material. For example, an artificial graphite and natural graphite are preferred. Especially the graphite that has embellished the negative-electrode-active-material particle surface with infinite form carbon etc. has the desirable generation of gas under charge from few things.

[0042]The analysis result by the X-ray diffraction etc. of the graphite which can be conveniently used for below is shown.;

size La 20nm of the microcrystal of lattice spacing ( $d_{002}$ ) 0.333-0.350nm a shaft orientations -- the above --

size Lc 20nm of the microcrystal of c shaft orientations -- the above -- true density 2.00 - 2.25 g/cm<sup>3</sup>. It is also possible to add metallic oxides, such as a tin oxidation thing and a silicon oxide, Lynn, boron, amorphous carbon, etc. to graphite, and to perform refining to it. It is possible to control electrolytic disassembly and to improve a battery characteristic by reforming the surface of graphite by the above-mentioned method especially, and it is desirable. What [ lithium metal content alloys such as a lithium metal, lithium aluminum, lithium lead, lithium tin, lithium aluminum tin, lithium gallium, and a Wood metal, etc. are used together for to graphite ], It is usable as negative electrode active material by returning electrochemically beforehand in the graphite etc. in which lithium was inserted.

[0043]As for the granular material of positive active material, and the granular material of a negative pole material, it is desirable that it is a mean grain size of 100 micrometers or less. As for especially the granular material of positive active material, it is desirable that it is 10 micrometers or less in order to improve the high-output characteristic of a nonaqueous electrolyte battery. A grinder and a classifier are used in order to obtain a granular material in predetermined shape. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a planetary ball mill, a jet mill, a turning air stream type jet mill, a screen, etc. are used. The wet milling which made organic solvents, such as water or hexane, live together at the time of grinding can also be used. As the classification method, there is no limitation in particular and a screen, a pneumatic elutriation machine, etc. are used if needed in dry type and a wet type.

[0044]As mentioned above, although the positive active material and the negative pole material which are the major constituents of an anode and a negative electrode were explained in full detail, in said anode and a negative electrode, a conducting agent, a binder, a thickener, a filler, etc. other than said major constituent may contain as other constituents.

[0045]If it is a electron conductive material which does not have an adverse effect on battery capacity as a conducting agent, will not be limited, but. Usually, natural graphite (flaky graphite, scaly graphite, earthy

graphite, etc.), an artificial graphite, Conductive materials, such as carbon black, acetylene black, Ketchen black, a carbon whisker, carbon fiber, metal powder (copper, nickel, aluminum, silver, gold, etc.), a metal fiber, and electrically-conductive-ceramics material, can be included as one sort or those mixtures.

[0046]In these, acetylene black is more desirable than the viewpoint of electron conductivity and coating nature as a conducting agent. As for the addition of a conducting agent, 0.1 % of the weight - 50 % of the weight are preferred to the gross weight of an anode or a negative electrode, and 0.5 % of the weight - 30 % of the weight are especially preferred. Since a required carbon content is reducible if especially acetylene black is ground and used for a 0.1-0.5-micrometer ultrafine particle, it is desirable. These mixing methods are physical mixing and the place made into the ideal is homogeneous mixing. Therefore, it is possible to mix the powder-mixing machine like a V shaped rotary mixer, a smooth S form mixer, a \*\*\*\*\* machine, a ball mill, and a planetary ball mill by dry type or a wet type.

[0047]As said binder, usually Polytetrafluoroethylene (PTFE), Thermoplastics, such as polyvinylidene fluoride (PVDF), polyethylene, and polypropylene, The polymer which has the rubber elasticity of an ethylene-propylene-diene terpolymer (EPDM), sulfonation EPDM, styrene butadiene rubber (SBR), fluorocarbon rubber, etc. can be used as one sort or two sorts or more of mixtures. As for the addition of a binder, 1 to 50 % of the weight is preferred to the gross weight of an anode or a negative electrode, and its 2 to 30 % of the weight is especially preferred.

[0048]As said thickener, polysaccharide, such as carboxymethyl cellulose and methyl cellulose, etc. can usually be used as one sort or two sorts or more of mixtures. As for the thickener which has a functional group which reacts to lithium like polysaccharide, it is desirable to methylate, for example and to deactivate the functional group. As for the addition of a thickener, 0.5 to 10 % of the weight is preferred to the gross weight of an anode or a negative electrode, and its 1 to 2 % of the weight is especially preferred.

[0049]It is [ anything ] good if it is the material which does not have an adverse effect on battery capacity as a filler. Usually, olefin system polymer, such as polypropylene and polyethylene, amorphous silica, alumina, zeolite, glass, carbon, etc. are used. 30 or less % of the weight of an addition is [ the addition of a filler ] preferred to the gross weight of an anode or a negative electrode.

[0050]An anode and a negative electrode are said granular materials (in the case of an anode). it is a granular material of positive active material -- the case of a negative electrode -- the granular material of a negative pole material -- it is -- after making organic solvents, such as N-methyl pyrrolidone and toluene, mix a conducting agent and a binder, the obtained mixed liquor is applied on the charge collector explained in full detail below, and it is suitably produced by drying. About said coating method, for example Roller coating, such as an applicator roll, Although it is desirable to apply to arbitrary thickness and arbitrary shape using means, such as screen coating, a doctor blade method, spin coating, and bar coater, it is not limited to these.

[0051]It is [ anything ] good if it is an electronic conductor which does not have an adverse effect in the constituted cell as a charge collector. For example, as a charge collector for anodes, it is the purpose of an adhesive property, conductivity, and oxidation-resistant improvement besides aluminum, titanium, stainless steel, nickel, baked carbon, a conductive polymer, electrically conductive glass, etc., The thing which processed the surfaces, such as aluminum and copper, with carbon, nickel, titanium, silver, etc. can be used. As a charge collector for negative electrodes, it is the purpose of raising the adhesive property,

conductivity, and reduction-proof nature else [ , such as copper, nickel, iron, stainless steel, titanium, aluminum, baked carbon a conductive polymer electrically conductive glass, and an aluminum-Cd alloy ], The thing which processed the surfaces, such as copper, with carbon, nickel, titanium, silver, etc. can be used. About such materials, it is also possible to oxidize the surface.

[0052]About the shape of a charge collector, the thing by which expanded one was carried out, the Russ object, film state, a sheet shaped, net shape and a punch or a porous body besides the shape of foil, a firing object, the organizer of a textiles group, etc. are used. Although there is no limitation in particular of thickness, a 1-500-micrometer thing is used suitably. It is preferred to use the alloy foil with which aluminium foil excellent in oxidation resistance is excellent in reduction-proof nature and conductivity, and includes cheap copper foil, nickel foil, iron foils, and those parts as a negative electrode as an anode in these charge collectors. It is preferred that split-face surface roughness is the foil more than 0.2micromRa, and, thereby, the adhesion of positive active material or negative electrode active material, and a charge collector becomes the outstanding thing. Therefore, since it has such a split face, it is preferred to use electrolytic foil. Especially the electrolytic foil that performed processing with Hana is the most preferred. the case where double-sided coating of the mixed liquor which mixed the above-mentioned positive active material or the negative pole material, the conducting agent, the binder, the organic solvent, etc. is carried out to this foil -- the surface roughness of foil -- the same -- or a, almost equal thing is desired.

[0053]It is preferred independent or to use together the porous membrane which shows the outstanding rate characteristic as a separator for nonaqueous electrolyte batteries, a nonwoven fabric, etc. As a material which constitutes the separator for nonaqueous electrolyte batteries, For example, the polyolefin system resin represented by polyethylene, polypropylene, etc., The polyester system resin represented by polyethylene terephthalate, polybutylene terephthalate, etc., Polyvinylidene fluoride, a fluoridation vinylidene-hexafluoropropylene copolymer, A fluoridation vinylidene-perfluoro vinyl ether copolymer, a fluoridation vinylidene-tetrafluoroethylene copolymer, A fluoridation vinylidene-trifluoro ethylenic copolymer, a fluoridation vinylidene-fluoro ethylenic copolymer, A fluoridation vinylidene-hexafluoroacetone copolymer, a fluoridation vinylidene-ethylenic copolymer, A fluoridation vinylidene-propylene copolymer, a fluoridation vinylidene-trifluoro propylene copolymer, a fluoridation vinylidene-tetrafluoroethylene hexafluoropropylene copolymer, a fluoridation vinylidene-ethylene-tetrafluoroethylene copolymer, etc. can be mentioned.

[0054]A strong viewpoint to below 98 volume % of the void content of the separator for nonaqueous electrolyte batteries is preferred. More than 20 volume % of the viewpoint of a charging and discharging characteristic to a void content is preferred.

[0055]The polymer gel which comprises polymer and electrolytes, such as acrylonitrile, ethylene oxide, propylene oxide, a methylmetaacrylate, vinyl acetate, vinyl pyrrolidone, and polyvinylidene fluoride, for example may be used for the separator for nonaqueous electrolyte batteries.

[0056]When the nonaqueous electrolyte in the nonaqueous electrolyte secondary battery of this invention is used by the gel state as mentioned above, it is desirable at the point which is effective in preventing a liquid spill.

[0057]When porous membrane, a nonwoven fabric, etc. which were mentioned above, and polymer gel are used together and used, since electrolytic solution retention of the separator for nonaqueous electrolyte batteries improves, it is desirable. That is, the film which covered parent solvent nature polymer several

micrometers or less thick on the surface and the fine hole wall surface of the polyethylene micropore film is formed, and said parent solvent nature polymer gels by making an electrolyte hold in the fine hole of said film.

[0058]The polymer etc. over which the acrylate monomer which has an ethylene oxide group, an ester group besides polyvinylidene fluoride, etc., the epoxy monomer, the monomer which has an isocyanate group, etc. constructed the bridge as said parent solvent nature polymer are mentioned. As for this monomer, it is possible to use a radical initiator together, to use heating and ultraviolet rays (UV) or to make crosslinking reaction perform using active light, such as an electron beam (EB), etc.

[0059]It can be used for intensity or the purpose of physical-properties control, being able to blend with said parent solvent nature polymer the physical-properties regulator of the range which does not block formation of a bridging body. As an example of said physical-properties regulator, inorganic filler {silicon oxide, titanium oxide, An aluminum oxide, magnesium oxide, zirconium oxide, a zinc oxide, Metallic carbonate [, such as metallic oxides, such as iron oxide, calcium carbonate, and magnesium carbonate, ]} and polymer {polyvinylidene fluoride, vinylidene fluoride / hexafluoropropylene copolymer, polyacrylonitrile, polymethylmethacrylate}, etc. are mentioned. The addition of said physical-properties regulator is usually 20 or less % of the weight preferably 50 or less % of the weight to a cross-linking monomer.

[0060]When it illustrates about said acrylate monomer, the unsaturated monomer of two or more organic functions is mentioned suitably, and more in an example. 2 organic-functions (meta) acrylate {ethylene glycol di(metha)acrylate, Propyleneglycol di(meth) acrylate, adipic acid and dineopentyl glycol S TERUJI (meta) acrylate, With a degree of polymerization [ of two or more ] poly ethylene glycol di(metha)acrylate, with a degree of polymerization [ of two or more ] poly propyleneglycol di(meth) acrylate, Di(meth)acrylate of a polyoxyethylene / polyoxypropylene copolymer, Butanediol di(metha)acrylate, hexamethylene GURIKORUJI (meta) acrylate}, etc., 3 organic-functions (meta) acrylate {TORIMECHI roll pro pantry (meta) acrylate, GURISERINTORI (meta) acrylate, the Tori (meta) acrylate of the ethylene oxide addition of glycerin, }, polyfunctional (meta) acrylate {pentaerythritol tetra (meta) acrylate of four or more organic functions, such as Tori (meta) acrylate of the propylene oxide addition of glycerin, ethylene oxide of glycerin, and Tori (meta) acrylate of a propylene oxide addition, Diglycerol hexa (meta) acrylate} etc. are mentioned. these monomers -- it can be independent, or it can use together and can use.

[0061]In said acrylate monomer, 1 organic-functions monomer can also be added for the purpose, such as physical-properties adjustment. As an example of said 1 organic-functions monomer, unsaturated-carboxylic-acid {acrylic acid, Methacrylic acid, crotonic acid, \*\*\*\* leather acid, vinylbenzoic acid, maleic acid, Boletic acid, itaconic acid, citraconic acid, mesaconic acid, methylenemalonic acid, } and unsaturation sulfonic acid {styrene sulfonic acid, acrylamide 2-methylpropanesulfonic acid}, etc., such as aconitic acid, or those salts (Li salt.) Na salt, K salt, ammonium salt, tetra-alkyl ammonium salt, etc., These unsaturated carboxylic acid Aliphatic series or alicyclic alcohol of C1-C18, what (methylmalate.) was selectively esterified by alkylene (C2-C4) glycol, polyalkylene (C2-C4) glycol, etc. what was selectively amidated by ammonia, such as mono- hydroxyethyl malate, the 1st class, or secondary amine (the maleic acid monoamide.) Ester of aliphatic series alcohol (methyl, ethyl, propyl, butyl, 2-ethylhexyl, stearyl, etc.) of acrylic ester (meta) [C1 - C18, such as N-methyl-maleic-acid monoamide and N,N-diethylmaleic acid monoamide, and acrylic acid (meta), or alkylene (C2-C4) glycol (ethylene glycol.) polyalkylene (C2-C4) glycols (a polyethylene glycol.),

such as propylene glycol and 1,4-butanediol Ester [ of a polypropylene glycol and acrylic acid (meta) ]]; (meta) Acrylamide or N-substitution (meta) acrylamide [(meta) acrylamide, ], such as N-methyl(meta) acrylamide and N-methylol(metha)acrylamide; Vinyl ester or allyl ester [vinyl acetate, ], such as allyl acetate; Vinyl ether or allyl ether [butylvinyl ether, ], such as dodecyl allyl ether; Unsaturated nitrile compound [(meta) acrylonitrile, ], such as croton nitril; Unsaturated alcohol [(meta) allyl alcohol] etc.; unsaturated amine [(meta) allylamine, ]; heterocyclic content monomers, such as a dimethylaminoethyl (meta) acrylic rate and diethylaminoethyl (meta) acrylate [N-vinyl pyrrolidone, vinylpyridine], etc.; Olefin system aliphatic hydrocarbon [ethylene, propylene, butylene, isobutylene, a pentene, (C6-C50)], such as alpha olefin; Olefin system alicyclic hydrocarbon [cyclopentene, ], such as a cyclohexene, cyclohepten, and norbornene; Olefin system aromatic hydrocarbon [styrene, ], such as; unsaturation imide [maleimide, such as alpha-methylstyrene and a stilbene; a containing halogen monomer [VCM/PVC, a vinylidene chloride, vinylidene fluoride, hexafluoropropylene], etc. are mentioned.

[0062]When it illustrates about said epoxy monomer, glycidylethers {bisphenol A diglycidyl ether, Bisphenol F diglycidyl ether, bromination bisphenol A diglycidyl ether, Phenol novolac glycidyl ether, cresolnovolak glycidyl ether}, etc., Glycidyl ester species {hexahydrophthalic acid glycidyl ester, }, glycidyl amines {triglycidyl isocyanurate, such as dimer acid glycidyl ester, }, such as a tetraglycidyl ether diamino phenylmethane, line aliphatic series epoxide {epoxidation polybutadiene, }, such as epoxidized soybean oil, and alicycle fellows epoxide {3, 4 epoxy-6 methylcyclohexylmethyl carboxylate, 3, and 4 epoxycyclohexylmethyl carboxylate} etc. are mentioned. These epoxy resins are independent, or they can be used, being able to add and stiffen a hardening agent.

[0063]As an example of said hardening agent, aliphatic polyamine {diethylenetriamine, Triethylenetetramine, 3,9-(3-aminopropyl)-2,4,8,10-TETORO oxaspiro [5, 5] undecane}, etc., Aromatic polyamine {meta xylenediamine, diamino phenylmethane}, etc. Polyamide {dimer acid polyamide} etc. acid anhydride {phthalic anhydride, Tetrahydro methylphthalic anhydride, hexahydro phthalic anhydride, trimellitic anhydride, Anhydrous methyl NAJIKKU acid}, phenols {phenol novolac} etc., Polymercaptan {polysulfide} etc., tertiary amines {tris(dimethyl aminomethyl) phenol, 2-ethyl-4-methylimidazole}, etc., a Lewis acid complex {boron trifluoride, ethylamine complex}, etc., etc. are mentioned.

[0064]When it illustrates about the monomer which has said isocyanate group, toluenediisocyanate, Diphenylmethane diisocyanate, 1, 6-hexamethylene diisocyanate, 2, 2, 4(2, 2, 4)-trimethyl hexamethylene diisocyanate, p-phenylenediisocyanate, 4,4'-dicyclohexyl methanediisocyanate, 3,3'-dimethyldiphenyl 4,4'-diisocyanate, dianisidinediisocyanate, M-xylenediisocyanate, trimethyl xylenediisocyanate, isophorone diisocyanate, 1,5-naphthalenediisocyanate, trans-1,4-cyclohexyldiisocyanate, lysine diisocyanate, etc. are mentioned.

[0065]In constructing a bridge, the monomer which has said isocyanate group Polyol and polyamine [bifunctional compound {water, Ethylene glycol, propylene glycol, a diethylene glycol, }, such as dipropylene glycol, 3 organic-functions compound {glycerin, trimethylolpropane, }, such as 1,2,6-hexanetriol and triethanolamine, 4 organic-functions compound {pentaerythritol, Ethylenediamine, tolylenediamine, diphenylmethanediamine, }, such as tetramethylolcyclohexane and methyl glucoside, 5 organic-functions compound {2,2,6,6-tetrakis (hydroxymethyl) cyclohexanol, }, such as diethylenetriamine, 6 organic-functions compound {sorbitol, mannitol, }, such as dulcitol, 8 organic-functions compound {sault cloth} etc.], and

polyether polyol (propylene oxide of said polyol or polyamine, and/or ethyleneoxide addition). The polyester polyol [aforementioned polyol, and a condensate with polybasic acid {adipic acid, o,m, para phthalic acid, succinic acid, azelaic acid, sebacic acid, and recinoleic acid}, polycaprolactone polyol {poly epsilon-caprolactone} etc., ], such as a polycondensation thing of hydroxycarboxylic acid, etc. can use together the compound which has active hydrogen.

[0066]A catalyst can be used together in said crosslinking reaction. When it illustrates about said catalyst, organotin compounds and trialkylphosphine. Amines [monoamine {N,N-dimethylcyclohexylamine, }, such as triethylamine, and annular monoamines {pyridine, N-methylmorpholine}, etc. Diamine {N,N,N',N'-tetramethylethylenediamine, N,N,N',N' - tetramethyl one -- 1,3 - butanediamine -- etc. --} -- triamine -- a class -- {-- N -- N -- N -- ' -- N -- ' - pentamethyl diethylenetriamine -- etc. --}. Hexamines {N,N,N' N'-tetra (3-dimethylaminopropyl)-methanediamine} etc. Those salts, such as annular polyamine {diazabicyclo octane (DABCO), N,N'-dimethylpiperazine, 1,2-dimethylimidazole, 1, and 8-diazabicyclo (5, 4, 0) undecene 7 (DBU)} etc., are mentioned.

[0067]Before laminating the separator for nonaqueous electrolyte batteries, an anode, and a negative electrode, or after the nonaqueous electrolyte secondary battery concerning this invention laminates an electrolyte, for example, it is poured in, and it is eventually produced suitably by closing with a sheathing material. As for an electrolyte, in the nonaqueous electrolyte battery around which an anode and a negative electrode wind the power generation element laminated via the separator for nonaqueous electrolyte batteries, it is preferred to pour in a power generation element before and after said winding. As a pouring-in method, it is possible to pour in by ordinary pressure, and it is usable also in a vacuum impregnating method or an application-of-pressure impregnation method.

[0068]As a material of the armor body of a nonaqueous electrolyte secondary battery, iron, a stainless steel, aluminum, a metal resin compound film, etc. which carried out the nickel plate are mentioned as an example. For example, the metal resin compound film of composition of having put the metallic foil with the resin film is preferred. If aluminum, iron, nickel, copper, stainless steel, titanium, gold, silver, etc. are foil without a pinhole as an example of said metallic foil, it will not be limited, but desirable lightweight and cheap aluminium foil is preferred. As a resin film by the side of a battery exterior, a polyethylene terephthalate film, Considering resin films which thrust and were excellent in intensity, such as a nylon film, as a resin film by the side of the inside of a cell, thermal melting arrival, such as a polyethylene film and a nylon film, is possible, and the film which has solvent resistance is preferred.

[0069]It is not limited in particular for the composition of a nonaqueous electrolyte secondary battery, and the coin cell and button cell which have a separator of an anode, a negative electrode and a monolayer, or a double layer, the cylindrical cell which has an anode, a negative electrode, and a rolled form separator further, a square-shaped cell, a flat type battery, etc. are mentioned as an example.

[0070]

[Example]This invention is not limited by the following statements although this invention is explained still in detail below based on an example.

[0071](Example 1) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 9:9:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt

was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 °C for 12 hours, it classified and was considered as  $D_{50}=20$ micrometer powder. The specific surface area measured with the BET adsorption method was  $0.90\text{m}^2/\text{g}$ .

[0072]As a result of the X-ray diffraction measurement by the CuK alpha rays of this powder, 2 theta, it turned out that a diffraction peak is observed in 18.56 degrees, 36.56 degrees, 37.76 degrees, 38.24 degrees, 44.32 degrees, 48.4 degrees, 58.4 degrees, 64.16 degrees, 64.8 degrees, and 68.8 degrees, and the high crystalline single phase considered to be the layer structure belonging to the space group R3m can be compounded. The X-ray diffraction figure of this powder is shown in drawing 1. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.45}\text{nickel}_{0.45}\text{Co}_{0.1}\text{O}_2$ .

[0073]Subsequently, the hue of this obtained powder was measured and it compared with the standard color chart. Measuring apparatus used for measurement of hue was set to Minolta Co., Ltd. make color leader CR10. As a reference of said measuring apparatus, JIS standard color chart YN-30 (Munsell value N3) was always used. A measurement result is a negative value of  $dL^*$  about the positive value of  $dL^*$ , and the blacker one in the one to said reference where brightness is whiter, In the positive value of  $da^*$ , it is a negative value of  $da^*$  about the one (the one where red is weaker) where green is strong in the one where hue is redder, and hue is given the more nearly yellow one with the positive value of  $db^*$ , and blue is given the strong one (the one where yellow is weaker) with the negative value of  $db^*$ .

[0074]In measuring powder, in order to take out the flat surface of said granular material, the powder for measurement has been arranged in said crevice of the sample holder of the aluminum board which provided the crevice, and the thin flat-surface quartz glass plate was covered in the upper part. When pressed down by said quartz glass plate, the quantity of the powder arranged in said crevice is sufficient quantity to such an extent that it does not produce the macroscopic opening of the grade which is seen from said quartz glass plate upper surface, and can be viewed between this aforementioned quartz glass plate and powder. And the undersurface of said quartz glass plate and the upper surface of said sample holder touched, and it was considered as the quantity which is not to such an extent that the crevice between the grades which are seen from the side and can be viewed did not arise.

[0075]In consideration of the sample upper surface being covered with a quartz glass plate, first, as reference measurement, the upper surface of JIS standard color chart YN-30 (it is the same as what was used for the reference side) installed what was covered with said flat-surface silica glass in the sample side of said measuring apparatus, and measured it. As a result, it was  $dL^*=+10.5$ ,  $da^*=-0.4$ , and  $db^*=+0.4$ . Next, in order to measure the value of a standard-for-comparison thing with measuring object powder, the upper part of JIS standard color chart Y05-30B (Munsell-value 5R3/1) installed and measured what was covered with said flat-surface silica glass to the sample side of said measuring apparatus as preliminary measurement. As a result, it was  $dL^*=+9.3$ ,  $da^*=+2.3$ , and  $db^*=+1.9$ .

[0076]Next, said powder was installed and measured by the above-mentioned method to the sample side of said measuring apparatus as this measurement. As a result, it was  $dL^*=+5.5$ ,  $da^*=+0.6$ , and  $db^*=+0.1$ .

[0077]Since the value of  $da^*$  showing hue and  $db^*$  is less than one, this result does not almost have a color

and is a gray system.

About the value of  $dL^*$  showing brightness, since the difference with the value of  $dL^*$  of said JIS standard color chart Y05-30B is -3.8, the thing brighter (whitish) than said JIS standard color chart Y05-30B is shown.

[0078] Since the value of  $da^*$  of JIS standard color chart Y05-30B measured by this method is +2.3 and the value of  $da^*$  of this powder is +0.6, the hue of this powder has a low chromaticity of a red direction as compared with JIS standard color chart Y05-30B.

[0079] The square-shaped nonaqueous electrolyte battery of capacity abbreviation 15Ah shown in drawing 2 as follows was produced using this powder as positive active material.

[0080] The polyvinylidene fluoride (PVDF) which is acetylene black and the binder which are the powder and conducting agent which are positive active material was mixed by the weight ratio 85:10:5, kneading dispersion of the N-methyl pyrrolidone was added and carried out as a solvent, and anode coating liquid was prepared. Solid content carried out weight conversion of said polyvinylidene fluoride as solid content using the solution by which dissolution distribution was carried out. Said anode coating liquid was applied to both sides of a 20-micrometer-thick aluminum foil charge collector, the whole thickness was adjusted to 230 micrometers, and the positive electrode sheet with the capacity of  $6.3 \text{ mAh/cm}^2$  was produced. Said positive electrode sheet was cut out in 61 mm in width, and 107-mm-high shape, an aluminum lead board 20 micrometers in thickness and 10 mm in width was attached to the end of a sheet, and it was considered as the anode board 7.

[0081] In addition, kneading dispersion of the polyvinylidene fluoride (PVDF) which is a binder was added and carried out for N-methyl pyrrolidone as a solvent to said negative pole material 10% of the weight, using an artificial graphite (particle diameter of 6 micrometers) as a negative pole material, and negative-electrode coating liquid was prepared. Solid content carried out weight conversion of said polyvinylidene fluoride as solid content using the solution by which dissolution distribution was carried out. Said negative-electrode coating liquid was applied to both sides of a 10-micrometer-thick copper foil charge collector, the whole thickness was adjusted to 180 micrometers, and the negative electrode sheet with the capacity of  $7 \text{ mAh/cm}^2$  was produced. Said negative electrode sheet was cut out in 65 mm in width, and 111-mm-high shape, a copper lead board 10 micrometers in thickness and 10 mm in width was attached to the end of a sheet, and it was considered as the negative electrode plate 9.

[0082] Reduced pressure drying of said anode board 7 and the negative electrode plate 9 was carried out at  $150^\circ\text{C}$  for 12 hours. Next, said anode board is inserted in the bag of the fine porous membrane made from polyethylene judged to 65 mm in width as the separator 8, and a 111-mm-high shaped bag, These were laminated by turns in order of the anode board 7 with the separator 8, and the negative electrode plate 9, and the electrode group which consists of the anode board 7 with the separator 8 of 40 sheets and the negative electrode plate 9 of 41 sheets was obtained.

[0083] Said electrode group was wrapped in to the insulating film which consists of polyethylene resin, it stored to the square-shaped battery case 10 made from aluminum, and the anode board 7 and the lead board of the negative electrode plate 9 were connected to the positive pole terminal 5 and the negative pole terminal 4 which were attached to the lid 2 made from aluminum which has the safety valve 1 with the bolt,

respectively. Subsequently, after embedding the preventive plate 6 of a laser omission at the square-shaped battery case 10, the lid 2 and the battery case 10 were made to fit in. It is insulated between said terminals 5 and 4 and said lid 2 by the gasket which consists of polypropylene resin.

[0084]In the laser welding part 3, laser welding of said lid 2 and the battery case 10 is carried out. In 25 \*\* after pouring in 65g of electrolysis solutions which carried out 1 mol/l dissolution of the  $\text{LiPF}_6$  and obturating them in said battery case 10 to the partially aromatic solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate, 1.5A and constant current constant potential charge of 4.2 V or 15 hours were performed, and constant current discharge of 1.5A and the final voltage 3V was performed. Thus, a square-shaped lithium cell 70 mm wide, 130 mm (terminal lump 136 mm in height) in height, and 22 mm in width was obtained.

[0085](Example 2) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 2:2:1 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 \*\* for 12 hours, it classified and was considered as  $D_{50}=20$ micrometer powder. The specific surface area measured with the BET adsorption method was  $0.93\text{m}^2/\text{g}$ .

[0086]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.4}\text{nickel}_{0.4}\text{Co}_{0.2}\text{O}_2$ .

[0087]It was set to  $dL^*=+3.5$ ,  $da^*=-0.1$ , and  $db^*=+0.1$  when the hue of this powder was measured by the same method as Example 1. Since the value of  $da^*$  of JIS standard color chart Y05-30B is +2.3 and the value of  $da^*$  of this powder is -0.1, the hue of this powder has a low chromaticity of a red direction as compared with JIS standard color chart Y05-30B.

[0088]The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0089](Example 3) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 1:1:1 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 \*\* for 12 hours, it classified and was considered as  $D_{50}=20$ micrometer powder. The specific surface area measured with the BET adsorption method was  $0.96\text{m}^2/\text{g}$ .

[0090]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.34}\text{nickel}_{0.33}\text{Co}_{0.33}\text{O}_2$ .

[0091]It was set to  $dL^*=+2.0$  and  $da^*=-0.2$  and  $db^*=-0.2$  when the hue of this powder was measured by the same method as Example 1. Since the value of  $da^*$  of JIS standard color chart Y05-30B is +2.3 and the

value of  $da^*$  of this powder is -0.2, the hue of this powder has a low chromaticity of a red direction as compared with JIS standard color chart Y05-30B.

[0092]The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0093](Example 4) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 3:3:4 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 °C for 12 hours, it classified and was considered as  $D_{50}=20$ micrometer powder. The specific surface area measured with the BET adsorption method was  $0.92\text{m}^2/\text{g}$ .

[0094]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.3}\text{nickel}_{0.3}\text{Co}_{0.4}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0095](Example 5) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 5:4:1 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 °C for 12 hours, it classified and was considered as  $D_{50}=20$ micrometer powder. The specific surface area measured with the BET adsorption method was  $0.92\text{m}^2/\text{g}$ .

[0096]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.5}\text{nickel}_{0.4}\text{Co}_{0.1}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0097](Example 6) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 4:5:1 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 °C for 12 hours, it classified and was considered as  $D_{50}=20$ micrometer powder. The specific surface area measured with the BET adsorption method was  $0.93\text{m}^2/\text{g}$ .

[0098]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate

analysis showed that the presentation of this powder was  $\text{LiMn}_{0.4}\text{nickel}_{0.5}\text{Co}_{0.1}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0099](Example 7) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 9:9:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 \*\* for 20 hours, it classified and was considered as  $D_{50}=20\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $0.3\text{m}^2/\text{g}$ .

[0100]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.45}\text{nickel}_{0.45}\text{Co}_{0.1}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0101](Example 8) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 9:9:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 \*\* for 5 hours, it classified and was considered as  $D_{50}=5\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $1.5\text{m}^2/\text{g}$ .

[0102]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.45}\text{nickel}_{0.45}\text{Co}_{0.1}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0103](Example 9) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 9:9:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 \*\* for 24 hours, it classified and was considered as  $D_{50}=5\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $0.25\text{m}^2/\text{g}$ .

[0104]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.45}\text{nickel}_{0.45}\text{Co}_{0.1}\text{O}_2$ . The square-shaped

lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0105](Example 10) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 9:9:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 \*\* for 3 hours, it classified and was considered as  $D_{50}=5\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $2.0\text{m}^2/\text{g}$ .

[0106]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.45}\text{nickel}_{0.45}\text{Co}_{0.1}\text{O}_2$ .

[0107]It was set to  $dL^*=+3.6$ ,  $da^*=+1.4$ , and  $db^*=+1.3$  when the hue of this powder was measured by the same method as Example 1. Since the value of  $da^*$  of JIS standard color chart Y05-30B is  $+2.3$  and the value of  $da^*$  of this powder is  $+1.4$ , the hue of this powder has a low chromaticity of a red direction as compared with JIS standard color chart Y05-30B. The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0108](Example 11) It agitated the atomic ratio of Mn:nickel:Co:B having mixed manganese nitrate, nickel nitrate, a cobalt nitrate, and boric acid so that 17:17:4:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 \*\* for 12 hours, it classified and was considered as  $D_{50}=9.0\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $0.9\text{m}^2/\text{g}$ .

[0109]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{B}_{0.05}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0110](Example 12) It agitated the atomic ratio of Mn:nickel:Co:aluminum having mixed manganese nitrate, nickel nitrate, the cobalt nitrate, and the aluminium nitrate so that 17:17:4:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 \*\* for 12 hours, it classified and was considered as  $D_{50}=9.3\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $0.9\text{m}^2/\text{g}$ .

[0111]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{aluminum}_{0.05}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0112](Example 13) It agitated the atomic ratio of Mn:nickel:Co:Mg having mixed manganese nitrate, nickel nitrate, the cobalt nitrate, and the magnesium nitrate so that 17:17:4:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 °C for 12 hours, it classified and was considered as  $D_{50}=9.3\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $0.9\text{m}^2/\text{g}$ .

[0113]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{Mg}_{0.05}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0114](Example 14) It agitated the atomic ratio of Mn:nickel:Co:Cr having mixed manganese nitrate, nickel nitrate, a cobalt nitrate, and chromium nitrate so that 17:17:4:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 °C for 12 hours, it classified and was considered as  $D_{50}=9.1\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $0.9\text{m}^2/\text{g}$ .

[0115]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{Cr}_{0.05}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0116](Example 15) It agitated the atomic ratio of Mn:nickel:Co:Fe having mixed manganese nitrate, nickel nitrate, a cobalt nitrate, and iron nitrate so that 17:17:4:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 °C for 12 hours, it classified and was considered as  $D_{50}=9.3\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $0.9\text{m}^2/\text{g}$ .

[0117]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high

crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{Fe}_{0.05}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0118](Example 16) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 9:9:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After adding lithium hydroxide powder to this mixed salt and calcinating under oxygen environment after mixing with a ball mill for 800 \*\* and 12 hours, it classified and was considered as  $D_{50}=5\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $3.5\text{m}^2/\text{g}$ .

[0119]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the layer structure was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.45}\text{nickel}_{0.45}\text{Co}_{0.1}\text{O}_2$ .

[0120]It was set to  $dL^*=-6.8$ ,  $da^*=+5.1$ , and  $db^*=+3.1$  when the hue of this powder was measured by the same method as Example 1. Since the value of  $da^*$  of JIS standard color chart Y05-30B is +2.3 and the value of  $da^*$  of this powder is +5.1, the hue of this powder has a high chromaticity of a red direction as compared with JIS standard color chart Y05-30B. The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0121](Comparative example 1) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 7:11:2 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 \*\* for 12 hours, it classified and was considered as  $D_{50}=20\text{micrometer}$  powder. The specific surface area measured with the BET adsorption method was  $0.97\text{m}^2/\text{g}$ .

[0122]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.35}\text{nickel}_{0.55}\text{Co}_{0.1}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0123](Comparative example 2) It agitated the atomic ratio of Mn:nickel having mixed manganese nitrate and nickel nitrate so that 1:1 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at 1000 \*\* for 12 hours, it classified and was considered as

$D_{50}=20$ micrometer powder. The specific surface area measured with the BET adsorption method was  $0.98\text{m}^2/\text{g}$ .

[0124]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.5}\text{nickel}_{0.5}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0125](Comparative example 3) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 11:11:18 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at  $1000^\circ\text{C}$  for 12 hours, it classified and was considered as  $D_{50}=20$ micrometer powder. The specific surface area measured with the BET adsorption method was  $0.90\text{m}^2/\text{g}$ .

[0126]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.275}\text{nickel}_{0.275}\text{Co}_{0.45}\text{O}_2$ .

[0127]The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0128](Comparative example 4) It agitated the atomic ratio of Mn:nickel:Co having mixed manganese nitrate, nickel nitrate, and a cobalt nitrate so that 53:37:10 might become comparatively, and having added this to nitric acid, and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. After having added lithium hydroxide powder to this mixed salt, calcinating after mixing with the ball mill and calcinating under oxygen environment at  $1000^\circ\text{C}$  for 12 hours, it classified and was considered as  $D_{50}=20$ micrometer powder. The specific surface area measured with the BET adsorption method was  $0.92\text{m}^2/\text{g}$ .

[0129]The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the high crystalline single phase believed to be the same layer structure as Example 1 was compoundable. Ultimate analysis showed that the presentation of this powder was  $\text{LiMn}_{0.53}\text{nickel}_{0.37}\text{Co}_{0.1}\text{O}_2$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like Example 1 was produced except having used this powder as positive active material.

[0130](Comparative example 5) It agitated having added manganese nitrate to nitric acid and applying heat, and was made to dissolve thoroughly. Next, nitric acid was evaporated and mixed salt was obtained. Lithium hydroxide powder was added to this mixed salt, it carried out after mixing with the ball mill, actual calcination was carried out under oxygen environment at  $850^\circ\text{C}$  for 3 hours, and powder was obtained. The X-ray diffraction measurement by the CuK alpha rays of this powder showed that the crystal which has Spinel structure was compoundable. Ultimate analysis showed that the presentation of this powder was

$\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ . The square-shaped lithium cell of capacity abbreviation 15Ah shown in drawing 2 like

Example 1 was produced except having used this powder as positive active material.

[0131](Battery capacity examination) Using the cell produced by the above each example and comparative example, the high rate discharge performance examination was done at the temperature of 25 \*\*, and the charge-and-discharge cycle performance examination was done succeedingly.

[0132]The conditions of the high rate discharge performance examination made charge the current 7.5A (0.5It) and the constant current constant potential charge of 4.3 V or 3 hours, and discharge was made into the constant current discharge of the current 1.5A (0.1It) or 30A (2It) and the final voltage 3.0V.

[0133]The conditions of the charge-and-discharge cycle performance examination made charge the current 7.5A (0.5It) and the constant current constant potential charge of 4.3 V or 3 hours, and discharge was made into the constant current discharge of the current 7.5A (0.5It) and the final voltage 3.0V. After charge and discharge, the rest mode for 10 minutes was inserted, respectively.

[0134]In the high-rate-discharge examination, the ratio to service capacity when it discharges with the current of 1.5A of service capacity when it discharges with the current of 30A was made into the high rate discharge performance value (%). In the charge-and-discharge cycle performance examination, service capacity made the cycle life the number of cycles when it fell even to 80% to the early service capacity which started said charge-and-discharge cycle performance examination. The result of such system performance testing is shown in Tables 1 and 2.

[0135](Peg test) Constant current constant potential charge of 15 hours was performed by 1.5A and 4.2V to the cell of Examples 1-6, and the peg test which makes the iron nail which has metallic luster with a diameter [ phi ] of 3 mm penetrate in the direction which intersects perpendicularly to the polar-plate side of a cell to two thirds of the thickness of a cell at 100 mm/second in speed was done. A result is combined with Tables 1 and 2, and is shown.

[0136]

[Table 1]

表1

正価法物質			組成式の充足					色調			電池性能		
製造条件	組成 (Li <sub>1-x</sub> (Mn <sub>1-x</sub> Ni <sub>x</sub> Co <sub>2</sub> Ni <sub>2</sub> )O <sub>2</sub> )	0.5 ≤ x ≤ 0.1	-0.1 ≤ y ≤ 0.1	y ≤ x + z + b	0 < z ≤ 0.4	0.5 ≤ x y	色調 d <sub>500</sub>	1. SA 法 電解液 電解量 (mAh/g)	30A 放 電容量 (mAh/g)	高電流 電性能 値 (%)	サイク ル寿命	釘刺し試験結果	
実施例1	1000℃ 12時間	○	○	○	○	○	+0.6	160	113	71	700	50℃、電解・充 水・白濁なし	
実施例2	"	○	○	○	○	○	-0.1	165	120	73	750	"	
実施例3	"	○	○	○	○	○	-0.2	165	135	82	750	60℃、電解・充 水・白濁なし	
実施例4	"	○	○	○	○	○	0.92	160	120	75	600	80℃、電解・充 水・白濁なし	
実施例5	"	○	○	○	○	○	0.92	155	101	65	600	50℃、電解・充 水・白濁なし	
実施例6	"	○	○	○	○	○	0.93	155	116	76	660	80℃、電解・充 水・白濁なし	
実施例7	1000℃ 20時間	○	○	○	○	○	0.3	160	112	70	600		
実施例8	1000℃ 5時間	○	○	○	○	○	1.5	160	114	71	700		
実施例9	1000℃ 24時間	○	○	○	○	○	0.25	160	94	59	720		
実施例10	1000℃ 3時間	○	○	○	○	○	+1.4	160	120	76	300		
実施例11	1000℃ 12時間	○	○	○	○	○	0.9	157	118	75			
実施例12	"	○	○	○	○	○	0.9	155	113	73			
実施例13	"	○	○	○	○	○	0.9	152	114	75			
実施例14	"	○	○	○	○	○	0.9	152	114	76			
実施例15	"	○	○	○	○	○	0.9	160	120	76			
実施例16	800℃ 12時間	○	○	○	○	○	+5.1	160	113	71	200		

[0137]

[Table 2]

表2	焼成条件	組成( $\text{Li}_{1-x}[\text{Mn}_x\text{Ni}_y\text{Co}_z\text{O}_2]$ )	正極活物質				負極活物質				サイクル試験結果		
			$0 \leq x \leq 0.1$ $y \leq 0.1$	$-0.1 \leq y \leq 0.1$ $z \leq 0.1$	$y \leq x + z$ $x + y \leq 0.4$	色相	比表面積 ( $\text{m}^2/\text{g}$ )	1.5A放電容量 (mAh/g)	30A放電容量 (mAh/g)	高率放電性能 (%)			
比較例1	1000℃ 12時間	$\text{LiMn}_{0.9}\text{Ni}_{0.05}\text{Co}_{0.05}\text{O}_2$	○	×	○	○	○	0.87	160	116	71	950	550℃、安全弁作動、白煙
比較例2	"	$\text{LiMn}_{0.9}\text{Ni}_{0.1}\text{O}_2$	○	○	○	×	○	0.98	140	85	61	500	50℃、過熱・発火、白煙なし
比較例3	"	$\text{LiMn}_{0.8}\text{Ni}_{0.2}\text{Co}_{0.0}\text{O}_2$	○	○	○	×	×	0.90	155	124	80	600	350℃、安全弁作動、白煙
比較例4	"	$\text{LiMn}_{0.7}\text{Ni}_{0.3}\text{Co}_{0.0}\text{O}_2$	○	×	○	○	○	0.92	140	77	55	400	50℃、過熱・発火、白煙なし
比較例5	850℃ 3時間	$\text{Li}_{1-x}\text{Mn}_x\text{Ni}_y\text{Co}_z\text{O}_4$	○	×	○	×	×	0.90	118	94	80	350	

[0138]Above-mentioned Table 1 and 2 shows the cell of this invention having large service capacity, having good high rate discharge performance and cycle performance, and excelling also in safety. Hereafter, each example and comparative example are considered in detail.

[0139](Effect of Co ingredient) As opposed to the cell of the comparative example 2 which used for positive active material the multiple oxide which does not contain Co, By the cell of Examples 1-10 and the cell of the comparative example 1 which were used for positive active material, the multiple oxide expressed with  $\text{Li}[\text{Mn}_x\text{Ni}_y\text{Co}_z]\text{O}_2$  which has Co ingredient. Probably because service capacity increased all substantially and the crystal structure became stable, a long time understands a cycle life.

[0140]( $y \leq x+z+b$ ,  $-0.1 \leq x-y \leq 0.1$ ) It is expressed with  $\text{Li}[\text{Mn}_x\text{Ni}_y\text{Co}_z]\text{O}_2$ , The big difference is not seen by a discharge characteristic and the cycle life if the effect of having changed composition ratio is compared about the cell of Examples 1-6 and the cell of the comparative examples 1-4 which used for positive active

material the multiple oxide whose specific surface area is almost the same.

[0141]However, in the empirical formula expressed with  $\text{Li}_{(1+a)}[\text{Mn}_x\text{nickel}_y\text{Co}_z\text{M}_b]\text{O}_2$  as a result of a peg test () [  $y \leq x+z+b$  and ] -In the cell of Examples 1-6 which is filling  $0.1 \leq x-y \leq 0.1$ , although it went up to 90 \*\* in the portion (namely, portion nearest to \*\*\*\*\*) with the largest cell lateral portion temperature, a burst, ignition, and generating of white smoke were not accepted. On the other hand, by the cell 1 of the comparative example 1 which is not filling ( $y \leq x+z+b$ ,  $-0.1 \leq x-y \leq 0.1$ ), lateral portion temperature rose to 550 \*\*, the safety valve opened, and generating of white smoke was accepted.

[0142]When the cell of Examples 5 and 6 which fulfills the conditions of ( $y \leq x+z+b$ ) was compared with the cell of the comparative example 4, the cell of the comparative example 4 with a large Mn content also has good safety, although a rise in heat is large, and a burst, ignition, and generating of white smoke were not accepted. However, there were many amounts of Mn, in the cell of the comparative example 4 which is not filling ( $-0.1 \leq x-y \leq 0.1$ ), it became what has the large internal resistance of a cell, and a result to which high rate discharge performance falls was brought.

[0143]( $0 < z \leq 0.4$ ,  $0.3 \leq x$ ,  $0.3 \leq y$ ) The cell of Examples 3 and 4, Although the capacity of 165 mAh/g was shown and high rate discharge performance has been improved when the cell of the comparative example 3 is compared, and the ratio of x:y:z is close to 1:1:1, when x and y were less than 0.3, and when z exceeded 0.4, the problem was produced at safety and it resulted in white smoke generating.

[0144]By thus, the thing which the composition ratio of the transition metal element which constitutes the multiple oxide expressed with  $\text{Li}_{(1+a)}[\text{Mn}_x\text{nickel}_y\text{Co}_z\text{M}_b]\text{O}_2$  changes. As a cause by which the safety of the cell which used it for positive active material is influenced, it guesses as follows. That is, nickel is considered that safety falls although the character of  $\text{LiNiO}_2$  is approached and capacity increases so that there is a tendency for a multiple oxide to become unstable thermally and composition ratio becomes large since there is an effect which extends between the layers of said multiple oxide. On the other hand, it is thought that it has an effect which offsets the thermal instability nature by nickel mentioned above since Mn is effective in cutting down between the layers of said multiple oxide. Co is conjectured to show said nickel and Mn middle in respect of thermal stability, and it seems that the problem by making composition ratio high is not produced since thermal stability is not sharply changed even if it changes composition ratio.

[0145](Influence of specific surface area) It is expressed with the same empirical formula  $\text{LiMn}_{0.45}\text{nickel}_{0.45}\text{Co}_{0.1}\text{O}_2$ . If the performance is compared about the cell of Examples 1, 7, 8, 9, and 10 which used for positive active material the multiple oxide in which specific surface areas differ, When there is a tendency for cycle performance to fall if specific surface area exceeds  $1.5\text{-m}^2/\text{g}$  and specific surface area is less than  $0.3\text{-m}^2/\text{g}$ , it turns out that there is a tendency for high rate discharge performance to worsen. From this, the nonaqueous electrolyte secondary battery which combines good cycle performance and high high rate discharge performance can be provided because below  $1.5\text{-m}^2/\text{g}$  carries out [ more than  $0.3\text{ m}^2/\text{g}$  ] the value of the specific surface area of a multiple oxide.

[0146]High rate discharge performance in the cell of the comparative example 3 using the manganic acid ghost which has the Spinel structure said to be good. Since the high rate discharging characteristic value shows 80% and a value as expected, it can check that there is no \*\*\*\* of the battery characteristic in the fuel

cell subsystem of this experiment in components other than anodes, such as an electrolysis solution and a negative electrode.

[0147](Effect of a different species element ingredient) In the cell of Examples 11-15 which used for positive active material the multiple oxide expressed with the empirical formula of  $\text{LiMn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{M}_{0.05}\text{O}_2$  which added different species elements M other than nickel, Mn, and Co to the presentation. Compared with the cell of Example 1 which has not added the different species element M, it turns out that each high rate discharge performance value is improving. Although it is not necessarily clear about this operation effect, it is thought that the substitution by a little different elements from nickel and Mn is effective in making lithium ion movement improve.

[0148]By the way, the cell of Example 11 which added boron was disassembled, and as a result of conducting ultimate analysis about each component which constitutes a cell, boron was detected from the negative electrode. rather than the effect of replacing the boron added at the time of composition by Mn and nickel, and stabilizing structure from this, rather, it is eluted from positive-active-material particles, the state of a positive electrode surface is changed into activity, and it is thought that the effect of raising high rate discharge performance is revealed.

[0149]As a result of performing same evaluation about  $\text{Li}_{1.1}[\text{Mn}_{0.4}\text{nickel}_{0.4}\text{Co}_{0.1}\text{O}_2]$  which made Li rich as  $a > 0$ , the effect that the characteristic was improvable as well as the case of other different species elements was checked. When Li is made rich, the tendency crystal growth becomes easy to carry out at the time of the calcination in an elevated temperature is obtained, and the effect that firing time can be shortened can also be checked. Therefore, when Li is made rich, it is thought that it is effective in helping crystallization at the time of calcination in addition to the effect which make Li-ion movement easy to carry out.

[0150]In the above-mentioned example, to the main constitution substance in positive active material,  $\text{Li}[\text{Mn}_{0.45}\text{nickel}_{0.45}\text{Co}_{0.1}\text{O}_2]$ ,  $\text{Li}[\text{Mn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{B}_{0.05}\text{O}_2]$ ,  $\text{Li}[\text{Mn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{aluminum}_{0.05}\text{O}_2]$ ,  $\text{Li}[\text{Mn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{Mg}_{0.05}\text{O}_2]$ ,  $\text{Li}[\text{Mn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{Cr}_{0.05}\text{O}_2]$ , Although  $\text{Li}[\text{Mn}_{0.425}\text{nickel}_{0.425}\text{Co}_{0.1}\text{Fe}_{0.05}\text{O}_2]$  and the cell using  $\text{Li}_{1.1}[\text{Mn}_{0.4}\text{nickel}_{0.4}\text{Co}_{0.1}\text{O}_2]$  were indicated, It is checked that an effect with the same said of the case where other elements are used is acquired.

[0151](Effect of hue) If battery capacity is compared about the cell of Examples 1, 10, and 16 which used for positive active material the multiple oxide in which it is expressed with the same empirical formula  $\text{LiMn}_{0.45}\text{nickel}_{0.45}\text{Co}_{0.1}\text{O}_2$ , and hue differs, The powder used for the cell of Example 16 which was 800 °C in calcination temperature is presenting dark brown appearance, In comparison with JIS standard color chart Y05-30B (Munsell-value 5R3/1), the value of  $da^*$  value of the multiple oxide powder used for the cell of Example 16 to the value+2.3 of  $da^*$  value of said standard color chart is +5.1, and its red is strong. Thus, when a multiple oxide with a high chromaticity of a red direction is used, it turns out that there is a tendency for service capacity to become low and for a cycle life to also become short.

[0152]Although the powder used for the cell of Example 10 was also presenting dark brown appearance, the value of  $da^*$  value of the powder used for the cell of Example 10 to the  $da^*$  value+2.3 of said standard color chart was +1.4 in comparison with JIS standard color chart Y05-30B (Munsell-value 5R3/1). Therefore, although it is inferior to the cell of Example 1 and a cycle life is slightly shorter than a cell, it turns out that

high capacity is maintained rather than the cell of Example 16.

[0153] Thus, the tendency for cycle life performance to fall was obtained in the cell using the powder in which red is shown strongly. When red was stronger as compared with JIS standard color chart Y05-30B (Munsell-value 5R3/1), the tendency for especially capacity to fall substantially was obtained. If the red of hue becomes strong, as a cause that cycle life performance falls, it is not necessarily clear, but calcination is not enough and it is considered as one of the causes that divalent Mn used for the raw material remains. Or it is also considered as one of the causes that the phase which contains tetravalent Mn by a certain cause is generating as an impurity. For this reason, a structural distortion is produced into the generated crystal and it is thought that cycle life performance is reduced.

[0154] It turned out that red becomes strong and a shows the fall of capacity, and the fall of cycle life performance when smaller than 0. It is thought that this is also depended on the same cause.

[0155] (Effect of a firing condition), changing some firing conditions on the basis of the firing condition of Example 1. If calcination temperature is less than 1000 °C as a result of advancing examination about the relation of the powdered hue and battery capacity which were obtained, as compared with JIS standard color chart Y05-30B (Munsell-value 5R3/1), red will become strong, and the fall of a cycle life will be regarded as having mentioned above. When calcination temperature was less than this tendency from 900 °C, the tendency to appear notably especially was seen.

[0156] When calcination temperature exceeded 1100 °C, the tendency for initial capacity to fall was seen. This is considered for an oxygen deficiency to occur in a crystal structure. In order to avoid such a phenomenon, at the time of the end of calcination, 5 hours or more can be spent on the temperature fall process from calcination temperature to ordinary temperature, and it can avoid by performing a loose temperature fall, but as for said calcination temperature, if productivity, energy expenditure, etc. are taken into consideration, it is preferred that it is 1100 °C or less.

[0157] Although cell lateral portion temperature rose in 50 °C - 90 °C as a result of doing the above mentioned peg test about Examples 8-16, a burst, ignition, and generating of white smoke were not accepted. Although not indicated in the above-mentioned example, when said calcination temperature was 1000 °C and firing time was made into less than 3 hours, probably because equalization by the rearrangement of a metallic element did not take place, each full width at half maximum in the X-ray diffraction figure by CuK alpha rays became large. The cell using this burned product brought a result to which service capacity falls about 20%, although a big difference was not seen by charging capacity compared with what made firing time 12 hours with the same calcination temperature. Therefore, as for firing time, it is preferred to consider it as 3 hours or more.

[0158]

[Effect of the Invention] the positive active material concerning claim 1 -- empirical formula  $\text{Li}_{1+a}$

$[\text{Mn}_x \text{nickel}_y \text{Co}_z \text{M}_b] \text{O}_2$  (M -- Mn.) Since it is expressed by elements other than nickel, Co, and Li and the coefficient in said empirical formula contains the multiple oxide which fills the above-mentioned expression of relations, it excels in high charge-and-discharge performance and charge-and-discharge cycle performance, and the positive active material which can produce the nonaqueous electrolyte secondary battery of the high energy density which has high safety can be provided.

[0159] Since a multiple oxide is obtained by being calcinated for 3 hours or more at not less than 900 °C the temperature of 1100 °C or less, the positive active material concerning claim 2 can provide the positive active material which can produce the nonaqueous electrolyte secondary battery excellent in especially initial capacity and charge-and-discharge cycle performance.

[0160] Since M is at least one sort of elements chosen from the group which consists of B, aluminum, Mg, Cr, and Fe, the positive active material concerning claim 3 can provide the positive active material which can produce the nonaqueous electrolyte secondary battery excellent in especially high rate discharge performance.

[0161] Since the specific surface area by the BET adsorption method of a multiple oxide is 0.3-1.5m<sup>2</sup>/g, the positive active material concerning claim 4 can provide the positive active material which can produce the nonaqueous electrolyte secondary battery excellent in especially a high rate discharging characteristic and charge-and-discharge cycle performance.

[0162] 2 theta of a powder X-ray diffraction figure for which the multiple oxide used CuK alpha rays the positive active material concerning claim 5 18.6° degree, Since it is a crystal structure which has a peak at 36.6° degree, 37.8° degree, 38.2° degree, 44.3° degree, 48.4° degree, 58.4° degree, 64.2° degree, 64.8° degree, and 68.8° degree, The positive active material which can produce the nonaqueous electrolyte secondary battery excellent in especially charge-and-discharge cycle performance can be provided.

[0163] The positive active material concerning claim 6 can provide the positive active material in which the hue of a multiple oxide can produce the nonaqueous electrolyte secondary battery with which especially the capacity of charge and discharge was secured certainly since the chromaticity of a red direction is low as compared with JIS standard color chart Y05-30B.

[0164] Since it is characterized by providing the anode, separator, and negative electrode which use positive active material concerning this invention as a major constituent according to the nonaqueous electrolyte secondary battery concerning claim 7, It excels in high charge-and-discharge performance and charge-and-discharge cycle performance, and the nonaqueous electrolyte secondary battery of the high energy density which has high safety can be provided.

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[Translation done.]